

Patent [Application] 2001-133064

[Document Name]       Specifications

[Title of the Invention] Porous Polymer Particle, Alkali-Resistant Anion Exchanger, Its Manufacturing Method, Ion Chromatography-Use Column and Anion Measurement Method

[Claims]

[Claim 1] A porous polymer particle that is characterized by a nitrogen containing heterocyclic group, which contains a quaternary ammonium structure, being bonded to an alkali-resistant polymer substrate by means of a spacer.

[Claim 2] A porous polymer particle as described in Claims 1 wherein a nitrogen containing heterocyclic group that contains a quaternary ammonium structure is derived from an aromatic or non-aromatic nitrogen containing heterocyclic compound.

[Claim 3] A porous polymer particle as described in Claim 2 wherein the nitrogen containing heterocyclic compound is a compound which can be selected from a group comprised of a pyridine compound that is represented by Formula (1)

[Chemical 1]

(In the formula, R represents an alkyl group or an alkoxy

group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group or halogen atom, or a halogen atom and m is an integer of 0-5. The plurality of R may be the same or different when m is 2 or more.),

a 1-alkylpyrrolidine compound that can be represented by Formula (2)

[Chemical 2]

(In the formula, R represents an alkyl group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group or a halogen group, R<sup>1</sup> represents an alkyl group or an alkoxy group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group and n is an integer of 0-2.),

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a 1-alkylpiperidine that is represented by Formula (3)

[Chemical 3]

(In the formula, R represents an alkyl group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group or a halogen atom, R<sup>1</sup> represents a hydroxyl group or an alkyl group or an alkoxy group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group, and p is an integer of 0-2.),

and a 1, 4-dialkylpiperidine compound that is represented by

Formula (4)

[Chemical 4]

(In the formula,  $R^2$  and  $R^3$  can be identical or different and, respectively, are hydrogen atoms, or alkyl groups of carbon number 1-5 that are also desirable when substituted by a hydroxyl group or halogen atom. However,  $R^2$  and  $R^3$  do not simultaneously represent hydrogen atoms.)

[Claim 4] A porous polymer particle as described in Claim 3 wherein a nitrogen-containing heterocyclic compound is pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-hydroxy-4-methylpyridine, 2-hydroxy-6-methylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, 1-methylpyrrolidine, 1-ethylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine, 1-(2-hydroxyethyl)piperidine, 1-(hydroxymethyl)piperidine, 1-(2-hydroxyethyl)pyrrolidine, 2-(2-hydroxyethyl)-1-methylpyrrolidine, 3-hydroxy-1-methylpiperidine, 4-hydroxy-1-methylpiperidine, 4-chloro-1-methylpiperidine, 1-(2-chloroethyl)piperidine, 1-(2-chloroethyl)pyrrolidine, 1-methylpiperidine,

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1-ethylpiperidine or 1, 4-dimethylpiperidine.

[Claim 5] A porous polymer particle as described in any of Claims 1 through 4 wherein the aforementioned porous polymer particle substrate is selected from poly(vinyl alcohol) type

copolymers and styrene/divinylbenzene type copolymers, the spacer molecule that connects the substrate and ion exchange group is a compound which contains a glycidyl group, and the aforementioned polymer is bonded with the spacer by means of a bond that does not cleave under alkali conditions.

[Claim 6] A porous polymer particle as described in any of Claims 1 through 5 that has an average particle size of 1-30  $\mu\text{m}$ .

[Claim 7] A porous polymer particle as described in any of Claims 1 through 6 that has an average pore size of 50-300 Å.

[Claim 8] An alkali-resistant anion exchanger that is made from a porous polymer particle as described in any of Claims 1 through 7.

[Claim 9] An alkali-resistant anion exchanger manufacturing method that is characterized by a spacer molecule that contains a glycidyl group being bonded to an alkali-resistant polymer porous particle that is selected from poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers by means of a bond which does not cleave under alkali conditions, and the introduction of an anion exchange group by reacting a nitrogen containing heterocyclic compound with the aforementioned glycidyl group.

[Claim 10] An alkali-resistant anion exchanger as described in Claim 9 wherein a nitrogen containing heterocyclic compound is selected from the nitrogen containing heterocyclic compounds that are described in Claims 2 or 3.

[Claim 11] An alkali-resistant anion exchanger manufacturing method as described in Claim 10 that is characterized

by a compound containing 2 or more glycidyl groups within the molecule being reacted with a poly(vinyl alcohol) type copolymer which is obtained by saponifying and partially converting a copolymer of a vinyl carboxylate and an isocyanurate type cross-linking monomer into a hydroxyl group, introducing a glycidyl group containing group such as the mass after the reaction becoming 103-140 when the mass of the aforementioned poly(vinyl alcohol) type copolymer is 100, and a nitrogen containing heterocyclic group being reacted with this.

[Claim 12] An alkali-resistant anion exchanger manufacturing method as described in Claim 11 with saponification of a poly(vinyl alcohol) type polymer

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performed until 0.5-5 meq/g of hydroxyl group is produced in the polymer.

[Claim 13] A suppressor system ion chromatography column-use packing that is made from an anion exchanger as described in Claim 8.

[Claim 14] A suppressor system ion chromatography-use column that is packed with anion exchanger as described in Claim 8.

[Claim 15] An anion measurement method by suppressor system ion chromatography with a column as described in Claim 14 and an alkali eluent used in combination.

[Claim 16] An anion measurement method as described in claim 15 wherein an alkali eluent is a hydroxide type eluent.

[Claim 17] An anion measurement method as described in

Claim 16 that uses a hydroxide type eluent at an isocratic condition of 20 mM or less as an alkali eluent.

[Claim 18] An anion measurement method as described in any of Claims 15 through 17 that is characterized by being used for measuring halogen oxide ions.

[Claim 19] An anion measurement method for non-suppressor system ion chromatography that is characterized by using a column packed with an anion exchanger as described in Claim 8 for measuring halogen oxide ions.

[Claim 20] An anion measurement method as described in Claim 18 or 19 wherein the halogen oxide ions are chlorite ions, chlorate ions and/or bromate ions.

[Claim 21] An anion measurement method as described in any of Claims 15 through 20 that is characterized by simultaneous measurement of the halogen oxide ions with anions that can be selected from a group comprised of fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, phosphate ions and sulfate ions.

[Claim 22] An anion measurement method as described in any of Claims 18 through 21 wherein the separation degree of the chlorite ions and bromate ions and the separation degree of the chlorate ions and the bromide ions, is 1.5 or greater.

[Claim 23] An anion measurement method as described in any of Claims 15 through 22 that is characterized by the fluoride ion peak not being superposed with the water dip position.

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[Claim 24]        An anion measurement method as described in any of Claims 15 through 23 that is characterized by the carbonate dip not being superposed with the anion peaks.

[Detailed Explanation of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

This invention pertains to a porous polymer particle, an alkali-resistant anion exchanger, its manufacturing method, a suppressor system ion chromatography column-use packing that is made from the anion exchanger, a suppressor system ion chromatography-use column and an anion measurement method that uses that column.

Also, when concretely stated, [this invention] pertains to a porous polymer particle, which can analyze inorganic anions like fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, and phosphate ions with good separation in a short retention time, under an isocratic (isocratic) condition with a constant concentration of hydroxide type eluent used, a suppressor system ion chromatography use alkali-resistant anion exchanger, its manufacturing method, a suppressor system ion chromatography-use column that uses that anion exchanger, and an anion measurement method that uses that column; further, [this invention] pertains to a measurement method that well separates and analyzes other inorganic anions (like fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions sulfate ions and phosphate ions) in a

short time, simultaneously with halogen oxide ions like chlorite ions, chlorate ions and bromate ions.

[0002]

[Background Art]

The analysis of 7 kinds of ions is important in analysis by water testing or the analysis of food: fluoride ions ( $F^-$ ), chloride ions ( $Cl^-$ ), nitrite ions ( $NO_2^-$ ), bromide ions ( $Br^-$ ), nitrate ions ( $NO_3^-$ ), sulfate ions ( $SO_4^{2-}$ ), phosphate ions ( $PO_4^{3-}$ ). These ions are called "7 Kinds of Standard Inorganic Anions". Currently, ion chromatography is utilized as an effective and highly accurate, highly sensitive means for analysis of inorganic anions that contain these 7 kinds of standard inorganic anions.

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[0003]

In ion chromatography, a sample which contains an ion species is injected into the column while an eluent is fed into the ion exchange column, the ions (kind, amount) that are separated out by the column by having differences in [their] retention times are detected by a high sensitivity detector like an electrical conductivity detector; this chromatography is a "suppressor system" that uses a suppressor or a "non-suppressor method" that does not use a suppressor. The suppressor is a device with a cation in the liquid displaced by a hydrogen ion, as shown in Figure 1, that is connected between the separation column and detector, and has the role of decreasing the background when an ion is detected by an electrical conductivity detector, thus increasing the measurement



sensitivity.

[0004]

Therefore, things like a mixed solution of sodium carbonate and sodium hydrogen carbonate, a boric acid buffer, an aqueous sodium hydroxide solution or an aqueous potassium hydroxide solution are passed through as the eluent in a "suppressor system" and ions are detected by a conductivity detector by means of a suppressor after the sample ions are separated by the separation column. The electrical conductivity that is measured by the detector is recognized as a signal superposed with the contribution from the ion species in the sample with the electrical conductivity of the eluent itself as the background, and the suppressor improves the measurement sensitivity of the signal for ion species in a sample by decreasing the background electrical conductivity by converting things like a salt or base in the eluent to things like an acid with a lower degree of dissociation.

A suppressor system requires an exclusive device as compared with a non-suppressor system, but this method is indispensable for regulating things like pure water and chemicals that are used in [fields] like the semiconductor field.

[0005]

Until now, the main anion exchangers which were used for suppressor system columns include pellicular type ion exchangers, which is coated with anion exchangeable latex coated after sulfonating a styrene/divinylbenzene type, and porous chemical bond type ion exchangers with an anion exchanger introduced to a

poly(vinyl alcohol) substrate.

[0006]

Pellicular type ion exchangers restrict the migration of ions to only the surface of the packing and do not allow the pores to be entered, thus, this ion exchanger has advantages such as (1) there being little diffusion and (2) the ion

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does not interfere with the substrate; however, there is the problem that the column efficiency is limited because the usable surface area of the packing is limited from the viewpoint of the structure. The column length must be increased or the particle size of the packing must be decreased in order to increase the column efficiency of pellicular type ion exchangers. However, the columns which are currently used already have a long length of 250 mm and further increase of the column length is impractical. A decrease in the particle size may be considered, but even packing with a particle size of approximately 5  $\mu$  m, which is commonly used in high-performance liquid chromatography, is difficult to manufacture because of limitations from the structure. Therefore, a pellicular type ion exchanger cannot meet the requirement of having a higher performance than the current theoretical plate number of 6,000 plates/column.

[0007]

However, this ion exchanger can realize higher performance than pellicular type ion exchangers of styrene/divinylbenzene type copolymer substrates because the porous chemical bond type ion

exchanger has an excellent effective surface area of the packing because the ions migrate into pores when ion exchange is carried out. These inventors proposed a porous chemical bond type ion exchanger derived from a poly(vinyl alcohol) substrate with an adequately high alkali-resistance even under the alkali conditions of anion analysis for suppressor methods and its manufacturing method (Publication of Japanese Laid-Open Patent No. 2001-40032). The obtainment of a high number of theoretical plates has the advantage of being able to control the position where a carbonate dip (carbonic acid gas, which is contained in the sample, is also detected as a carbonate ion when analyzing an anion by ion chromatography; here, that carbonate ion peak is called the carbonate dip.) appears in analysis which uses a column that is packed with this anion exchanger.

[0008]

Usually, the ideal in anion analysis by ion chromatography is balancing good separation with a limited short analysis time insofar as possible for the 7 kinds of standard inorganic anions. However, fluoride ions are difficult to retain on an anion exchanger in a separation column and quickly pass through the column. The result is that the separation of the signal peak due to the fluoride ion and the water dip (a negative peak that is generated by the eluent being diluted due to the injection of a sample) becomes inadequate and the measurement precision easily deteriorates.

The use of eluents with weak elution strength may be

considered for improving the retention of fluoride ions,

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but, in this case, a lengthening of the analysis time occurs due to extreme lengthening of the elution time of divalent or higher valence anions (sulfate ions and phosphate ions). In particular, this problem is extreme when the eluent is alkaline. Thus, the process must be [possible] in analysis conditions for simultaneous analysis of fluoride ions and divalent or higher valence anions.

[0009]

Therefore, a method that overcomes the above-mentioned problems by optimizing the eluent composition was investigated. For example, a method was disclosed wherein boric acid is added to a weakly acidic mobile phase in a non-suppressor system and anionic compounds are generated by selective reaction of this boric acid with fluoride ions, and the retention is improved (Publication of Japanese Examined Patent No. H7-37972). Further, the improvement of fluoride ion retention by varying the respective composition ratios when a mixed solution of sodium carbonate and sodium hydrogencarbonate is used as the eluent in a suppressor system is known. Also, a method with a salt of boric acid added to the eluent in a suppressor system was also disclosed (Publication of Japanese Laid-Open Patent No. 2000-180429). When the eluent can be composed of a plurality of components like this, there are corresponding possibilities by varying the composition.

[0010]

However, hydroxide type eluents like aqueous sodium hydroxide

solution and aqueous potassium hydroxide solution, which are used as eluents of suppressor systems, cannot overcome the problems for elution because, usually, a single component is utilized; thus, a specific means must be used for measurement in order to realize the improvement of both the retention of fluoride ions and the shortening of the elution time of divalent or higher valency anions (in particular, phosphate among the 7 kinds of standard inorganic anions) in suppressor systems that use alkaline eluents like this.

Methods performed in prior [art] are in 2 groups, one is a gradient analysis method that uses concentration gradient for the eluent and the other one is a method that uses a high concentration eluent of approximately 40 mM by establishing a large ion exchange capacity of the ion exchanger that is packed in the column.

[0011]

However, the first method has problems like requiring the application of at least 2 types of solutions that have different concentrations for imparting a concentration gradient and equipment and operations that absorb and mix these by using 2 pumps; also, there is the requirement of a stabilizing time until the eluent concentration returns to the origin[al concentration] for each measurement.

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Further, the second method has problems such as shortening the suppressor life by requiring high voltage for the electrodialysis by a suppressor apparatus that uses a continuous regeneration type of ion exchange membrane, which is currently widely utilized, due

to the eluent concentration being high.

[0012]

Further, not only are both the improvement of the retention of the above-mentioned fluoride ion and the shortening of the elution time of the phosphate ion when analyzing tap water realized by a suppressor system that uses a hydroxide type eluent, but the adequate separation of the chloride ions and nitrite ions is simultaneously realized. This is because analysis of nitrite ions to an extent of a number of ppb in the presence of a number of tens of ppm of chloride ions is necessary in tap water analysis. The simultaneous realization of the analysis of a trace amount of nitrite ions is complex because the separation of chloride ions and nitrite ions is inadequate since, even if adequate, carbonate ions elute between [those] by prior [art] columns that are used with hydroxide type eluents.

[0013]

The inventors previously proposed a manufacturing method for an anion carrier that is obtained by introducing a tertiary heterocyclic amine into an acrylate or methacrylate type polymer by means of a spacer and a column that was packed with this (Publication of Japanese Laid-Open Patent No. 2000-221179). However, this is a non-suppressor type ion chromatography-use column that uses an acidic eluent and a method of manufacturing the packing material, and is not one that measures anions with a suppressor type ion chromatography-use column that uses an alkaline eluent.

Most recently, the necessity of the analysis of halogen oxides like bromate ions, chlorite ions and chlorate ions has increased in addition to that of the inorganic ions that was previously performed for water supply analysis accompanying an increase in advanced water purification facilities.

[0014]

*IonPac As9-HC*, *IonPac AS9-SC* and *IonPac AS12A* are already commercially available from Dionex Corporation (*Dionex Corporation*) for use in suppressor system columns for the analysis of these halogen oxide ions. However, the column packing has a styrene/divinylbenzene type copolymer as a substrate and a quaternary alkylamine introduced as the anion exchange group.

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[0015]

However, until now, suppressor system columns, which are packed with porous chemical bond type ion exchanger with an anion exchanger introduced to a poly(vinyl alcohol) type substrate, were not known that could simultaneously separate and analyze the 7 types of inorganic anions fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, sulfate ions and phosphate ions with bromate ions, chlorite ions and chlorate ions. The separation degree  $R$  as the index for separation is determined by the following formula. Until now, a separation degree  $R$  of chlorite ions and bromate ions and a separation degree  $R$  of chlorate ions and bromide ions, simultaneously, being 1.5 or greater was difficult. (In general, the separation  $R$  degree is desired to be 1.5 or greater.)

[0016]

[Equation 1]

$$R=2X(t_2-t_1)/(w_1+w_2)$$

Here,  $w_1$  and  $w_2$  represent respective peak widths and  $t_1$  and  $t_2$  represent the respective retention times.

[0017]

[Problems to be Solved by the Invention]

This invention, in view of such circumstances, has the objective of offering an ion exchanger of ion chromatography use that can suppress the elution time of the phosphate ions to a short time of ten minutes—a number of tens of minutes without being done by gradient analysis (that is, under isocratic conditions of a constant concentration) by using a low concentration (for example, 20 mM or less) eluent in a suppressor system ion chromatography that uses a hydroxide type eluent, adequately separate fluoride ions, which are difficult to retain, from the water dip, and adequately separate the chloride ions and nitrite ions, its manufacturing method, a suppressor system ion chromatography column-use packing that uses this anion exchanger, an ion chromatography-use column and a precise anion measurement method at low cost that uses this column, and a measurement method that can simultaneously separate and analyze halogen oxide ions like bromate ions, chlorite ions and chlorate ions with

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the 7 kinds of standard inorganic anions of fluoride ions, chloride



ions, nitrite ions, bromide ions, nitrate ions, sulfate ions and phosphate ions.

[0018]

[Means for Solving the Problems]

These inventors attained the realization of this invention by discovering that the 7 kinds of standard inorganic anions can be well separated by using a column that is packed with alkali-resistant high strength anion exchanger which is made from a porous polymer which uses a structure with a nitrogen containing heterocyclic group, which contains a quaternary ammonium structure, bonded to an alkali resistant polymer substrate by means of a spacer without gradient analysis for the suppressor system ion chromatography which uses a hydroxide type eluent, and can simultaneously separate and analyze bromate ions, chlorite ions and chlorate ions, with the 7 kinds of inorganic ions of fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, sulfate ions and phosphate ions, as the result of diligent research that solves the above-mentioned problems.

[0019]

That is, this invention pertains to porous polymer particles, an alkali-resistant anion exchanger, its manufacturing method, a suppressor system ion chromatography column-use packing material that is made from this anion exchanger, a suppressor system ion chromatography-use column and an anion measurement method that uses this column.

[0020]

1. A porous polymer particle that is characterized by a nitrogen containing heterocyclic group, that contains a quaternary ammonium structure, being bonded to an alkali resistant polymer substrate by means of a spacer.

2. A porous polymer particle as described in the above-mentioned 1 wherein a nitrogen containing heterocyclic group that contains a quaternary ammonium structure is derived from an aromatic or non-aromatic nitrogen containing heterocyclic compound.

3. A porous polymer particle as described in the above-mentioned 2 wherein the nitrogen containing heterocyclic compound is a compound which can be selected from a group comprised of a pyridine compound that is represented by Formula (1)

[Chemical 5]

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(In the formula, R represents an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or halogen atom, or a halogen atom and m is an integer of 0~5. The plurality of R may be the same or different when m is 2 or more.),

a 1-alkylpyrrolidine compound that can be represented by Formula (2)

[Chemical 6]

(In the formula, R represents an alkyl group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group or a halogen group,  $R^1$  represents an alkyl group or an alkoxy group of carbon number 1-5 that is also desirable when substituted with a hydroxyl group and n is an integer of 0-2.),

a 1-alkylpiperidine that is represented by Formula (3)

[Chemical 7]

(In the formula, R represents an alkyl group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group or a halogen atom,  $R^1$  represents a hydroxyl group or an alkyl group or an alkoxy group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group and n is an integer of 1-2.),

and a 1, 4-dialkylpiperidine compound that is represented by Formula (4)

[Chemical 8]

(In the formula,  $R^2$  and  $R^3$  can be identical or different and, respectively, are hydrogen atoms, or alkyl groups of carbon number 1-5 that are also desirable when substituted by a hydroxyl group or halogen atom.

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However,  $R^2$  and  $R^3$  do not simultaneously represent hydrogen atoms.)

4. A porous polymer particle as described in the above-mentioned 3 wherein a nitrogen-containing heterocyclic compound is pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-hydroxy-4-methylpyridine, 2-hydroxy-6-methylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, 1-methylpyrrolidine, 1-ethylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine, 1-(2-hydroxyethyl)piperidine, 1-(hydroxymethyl)piperidine, 1-(2-hydroxyethyl)pyrrolidine, 2-(2-hydroxyethyl)-1-methylpyrrolidine, 3-hydroxy-1-methylpiperidine, 4-hydroxy-1-methylpiperidine, 4-chloro-1-methylpiperidine, 1-(2-chloroethyl)piperidine, 1-(2-chloroethyl)pyrrolidine, 1-methylpiperidine, 1-ethylpiperidine or 1, 4-dimethylpiperidine.

5. A porous polymer particle as described in any of the above-mentioned 1 through 4 wherein the aforementioned porous polymer particle substrate is selected from poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers, the spacer molecule that connects the substrate and ion exchange group is a compound which contains a glycidyl group, and the aforementioned polymer is bonded with the spacer by means of a bond that does not cleave under alkali conditions.

6. A porous polymer particle as described in any of the above-mentioned 1 through 5 that has an average particle size of 1-30  $\mu\text{m}$ .

7. A porous polymer particle as described in any of the above-mentioned 1 through 6 that has an average pore size of 50-300  $\text{\AA}$ .

8. An alkali-resistant anion exchanger that is made from a porous polymer particle as described in any of the above-mentioned 1

through 7.

9. An alkali-resistant anion exchanger manufacturing method that is characterized by a spacer molecule that contains a glycidyl group being bonded to an alkali-resistant polymer porous particle that is selected from poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers by means of a bond which does not cleave under alkali conditions, and the introduction of an anion exchange group by reacting a nitrogen containing heterocyclic compound with the aforementioned glycidyl group.

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10. An alkali-resistant anion exchanger as described in the above-mentioned 9 wherein a nitrogen containing heterocyclic compound is selected from the nitrogen containing heterocyclic compounds that are described in the above-mentioned 2 or 3.

11. An alkali-resistant anionic exchanger manufacturing method as described in the above-mentioned 10 that is characterized by a compound containing 2 or more glycidyl groups within the molecule being reacted with a poly(vinyl alcohol) type copolymer which is obtained by saponifying and partially converting a copolymer of a vinyl carboxylate and an isocyanurate type cross-linking monomer into a hydroxyl group, introducing a glycidyl group containing group such as the mass after the reaction becoming 103~140 when the mass of the aforementioned poly(vinyl alcohol) type copolymer is 100, and a nitrogen containing heterocyclic group being reacted with this.

12. An alkali resistant anion exchanger manufacturing method

as described in the above-mentioned 11 with saponification of a poly(vinyl alcohol) type polymer performed until 0.5~5 meq/g of hydroxyl group is produced in the polymer.

13. A suppressor system ion chromatography column-use packing that is made from an anion exchanger as described in the above-mentioned 8.

14. A suppressor system ion chromatography-use column that is packed with anion exchanger as described in the above-mentioned 8.

15. An anion measurement method by suppressor system ion chromatography with a column as described in the above-mentioned 14 and an alkali eluent used in combination.

16. An anion measurement method as described in the above-mentioned 15 wherein an alkali eluent is a hydroxide type eluent.

17. An anion measurement method as described in the above-mentioned 16 that uses a hydroxide type eluent at an isocratic condition of 20 mM or less as an alkali eluent.

18. An anion measurement method as described in any of the above-mentioned 15 through 17 that is characterized by being used for measuring halogen oxide ions.

19. An anion measurement method for non-suppressor system ion chromatography that is characterized by using a column packed with an anion exchanger as described in the above-mentioned 8 for measuring halogen oxide ions.

20. An anion measurement method as described in the above-mentioned 18 or 19 wherein the halogen oxide ions are chlorite ions, chlorate ions and/or bromate ions.

21. An anion measurement method as described in any of the above-mentioned 16 through 20 that is characterized by simultaneous measurement of the halogen oxide ions with anions that can be selected from a group comprised of fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, phosphate ions and sulfate ions.

22. An anion measurement method as described in any of the above-mentioned 18 through 21 wherein the separation degree of the chlorite ions and bromate ions and the separation degree of the chlorate ions and the bromide ions, is 1.5 or greater.

[0021]

[Actual Embodiment of the Invention]

This invention is explained in detail, below.

(A) Compound that Contains a Nitrogen Containing Heterocyclic Group

An aromatic or non-aromatic nitrogen containing heterocyclic compound is used as the raw material of the nitrogen containing heterocyclic group which has a quaternary ammonium structure. These compounds are also fine as having a substituent on the ring forming carbon atoms insofar as an obtained anion exchanger can function.

The (substituted) pyridine compounds that are represented by the following Formula (1) can be included as aromatic nitrogen containing heterocyclic compounds.

[0022]

[Chemical 9]

In Formula (1), R represents an alkyl group or alkoxy group of carbon number 1-5 that is also desirable when substituted by a hydroxyl group or a halogen atom, or a halogen atom, and m is an integer of 0-5. When m is greater than 2, the plurality of R may be identical or different.

Further, 1-(substituted) alkylpyrrolidine compounds that are represented by the following Formula (2), 1-(substituted) alkylpiperidine [compounds] which are represented by Formula (3) and 1-4-di(substituted) alkylpiperidine [compounds] that are represented by Formula (4) can be included as non-aromatic nitrogen containing heterocyclic compounds.

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[0023]

[Chemical 10]

[0024]

In Formula (2), R represents an alkyl group of carbon number 1-5 which is also desirable when substituted by a hydroxyl group or a halogen atom, R<sup>1</sup> represents a hydroxyl group or an alkyl group or



an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and n is an integer of 0~2.

[0025]

[Chemical 11]

[0026]

In Formula (3), R represents an alkyl group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group or a halogen atom,  $R^1$  represents a hydroxyl group or an alkyl group or an alkoxy group of carbon number 1~5 that is also desirable when substituted by a hydroxyl group and p is an integer of 0~2.

[Chemical 12]

[0027]

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In Formula (4),  $R^2$  and  $R^3$  are desirable as being identical or different and are respectively, a hydrogen atom, or an alkyl group of carbon numbers of 1~5 that is also desirable when substituted by a hydroxyl group or a halogen atom. Further,  $R^2$  and  $R^3$  do not simultaneously represent a hydrogen atom.

[0028]

Concrete examples of aromatic nitrogen containing heterocyclic

compounds includes ones like pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-hydroxy-4-methylpyridine, 2-hydroxy-6-methylpyridine, 2-hydroxypyridine, 3-hydroxypyridine and 4-hydroxypyridine.

Further, the nitrogen containing heterocyclic ring of these non-aromatic nitrogen containing heterocyclic compounds can contain organochemically allowable oxygen or sulfur instead of carbon. For example, compounds represented by Formula (5),

[Chemical 13]

Formula (6)

[Chemical 14]

Formula (7),

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[Chemical 15]

Formula (8)

[Chemical 16]

can be included. (In these formulas, R, R<sup>1</sup>, n, p are as aforementioned.)

[0029]

Concrete examples of non-aromatic nitrogen containing heterocyclic compounds include ones like 1-methylpyrrolidine, 1-ethylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine, 1-(2-hydroxyethyl)piperidine, 1-(hydroxymethyl)piperidine, 1-(2-hydroxyethyl)piperidine, 2-(2-hydroxyethyl)-1-methylpyrrolidine, 3-hydroxy-1-methylpiperidine, 4-hydroxy-1-methylpiperidine, 4-chloro-1-methylpiperidine, 1-(2-chloroethyl)piperidine, 1-(2-chloroethyl)pyrrolidine, 1-methylpiperidine, 1-ethylpiperidine 1-methyl-2-hydroxyethyl)morpholine and 1,4-dimethylpiperidine.

[0030]

(B) Anion Exchanger and Its Manufacturing Method

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The amount of the anion exchange group that is introduced is desirably 4~200  $\mu\text{eq/g}$ , and more desirably 8~50  $\mu\text{eq/g}$ .

Ones like alkali-resistant porous chemical bond type ion exchangers and pellicular type ion exchangers can be included as embodiments of the packing material that is manufactured by

introducing the above-mentioned ion exchange group.

[0031]

(1) Porous Chemical Bond Type Ion Exchangers

Porous chemical bond type ion exchangers that can be suitably used in this invention are ones with ion exchange groups by bonding the above-mentioned nitrogen containing heterocyclic compounds to an alkali-resistant polymer by means of a spacer.

[0032]

The porous polymers that can be used as the porous chemical bond type ion exchanger substrate are not particularly limited when [they are] alkali-resistant. Ones like poly(vinyl alcohol) type copolymers and styrene/divinylbenzene type copolymers can be included as examples of this kind of polymer.

The spacer molecule, which has a group that is capable of bonding with a tertiary heterocyclic amine compound, is bonded to these alkali-resistant porous polymers and an ion exchange group is produced by then reacting a tertiary heterocyclic amine compound with this.

[0033]

The spacer molecule provides a plurality of atoms between the substrate surface and ion exchange group, usually more than 3 atoms and less than 20, and is bonded with the alkali resistant porous polymer at one end and with the ion exchange group at the other end. The result is that [the molecule] acts as a spacer which lengthens the distance between both parties and has the function of controlling peak diffusion by suppressing ion-substrate

interference.

Compounds that contain a glycidyl group which bonds with tertiary heterocyclic amine compounds are desirable as spacer molecules. Ones like epichlorohydrin, 1,4-butanediol diglycidyl ether, ethylene glycol diglycidyl ether and glycerol glycidyl ether can be included as concrete examples.

[0034]

(2) Porous Chemical Bond Type Ion Exchanger Manufacturing Method

The bond of the spacer molecule with the alkali-resistant porous polymer is desirable when cleaving does not at pH conditions used in anion analysis.

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The manufacturing method is not particularly limited, but manufacturing can be by methods where an ester bond is contained in an alkali-resistant porous polymer and reacted with a diglycidyl compound which contains 2 or more glycidyl groups in the same molecule as the spacer molecule, with a hydroxyl group from saponifying this [polymer], for example. The schematic below shows one example of a 1-methylpiperidine introduced to a hydroxyl group of a substrate by means of 1,4-butanediol diglycidyl ether as a spacer.

[0035]

[Chemical 17]

[0036]

When [this method] is concretely explained in detail by taking an alkali-resistant poly(vinyl alcohol) type copolymer as an example, one part of the ester group of the copolymer is converted to a hydroxyl group by saponifying the copolymer with a vinyl carboxylate and a cross-linkable monomer that has an isocyanurate ring. The hydrophilicity of the substrate is increased and the interference with the ion is controlled by this, and the hydroxyl group becomes an active site necessary for reaction with the spacer molecule. A compound that contains 2 or more glycidyl groups within the same molecule, like 1,4-butanediol diglycidyl ether, is reacted with this.

[0037]

The saponification is desired to be such that the hydroxyl group is present as at least 0.5 meq/g or more but 5 meq/g or less, desirably 1.0~3 meq/g, for adequate introduction of the glycidyl group containing group that reacts with a tertiary heterocyclic amine. Introduction of the required glycidyl group containing group becomes difficult when the hydroxyl group is less than 0.5 meq/g, as does improving the performance of the column because the particle size of the substrate decreases by decreasing the strength of the substrate when 5 meq/g is exceeded, thus [both cases] are undesirable.

[0038]

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The amount of hydroxyl group is determined by reacting the

hydroxyl group with acetic anhydride and determining the amount of anhydrous acetate that is consumed or the change in the weight after the reaction. At this time, determination can be by the above-mentioned methods after functional group is protected for cases where the functional group of the substrate also reacts. The amount of hydroxyl group, when 1 g of dried substrate is reacted with 1 mmol of acetate anhydride, is 1 mmol/g.

[0039]

Further, the vinyl carbonate that is preferably used in this method is a compound that has one or more polymerizable carbonate vinyl ester groups and ones like, for example, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate and vinyl pivalate can be included. These can be used independently or by combining two or more types. Among these, vinyl acetate and vinyl propionate, which are hydrophilic and facilitate polymerization and saponification, are preferably used.

[0040]

Cross-linking monomers that have isocyanurate rings which are represented by the following general formula can be included as preferred examples of an isocyanurate type cross-linking monomer.

[Chemical 18]

[0041]

(In the formula,  $R^4$ ,  $R^5$  and  $R^6$ , respectively and independently, represent  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ,  $-\text{CH}_2-\text{C}\equiv\text{CH}$  or  $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$ ). In this, triallyl cyanurate with  $R^4$ ,  $R^5$  and  $R^6$  all being  $-\text{CH}_2\text{CH}=\text{CH}_2$  is preferred as a cross-linking agent with good copolymerizability with vinyl acetate and high stability even for saponification.

[0042]

The mass increase after the glycidyl compound reaction,

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when the mass of the poly(vinyl alcohol) type copolymer is 100, is 103-140. The mass increase is not desired to be less than 103 because the alkali resistance is becomes inadequate, but exceeding 140 is undesirable because the particles become soft and the association of the particles themselves occurs. The mass increase after the glycidyl compound reaction is desired to be 104-135, more desirably 105-125.

[0043]

The anion exchanger obtained by the above-mentioned method is a porous particle. The pore size of the porous particle is 50-300 Å, desirably 50-150 Å, and more desirably 50-100 Å. The pore size being less than 50 Å is not desirable because the introduction of the glycidyl group containing group to inside the pores becomes difficult. Exceeding 300 Å is not desirable because the strength of the particles is decreased. Method that are generally used for high-performance liquid chromatography packing materials are used for controlling the particle size.

[0044]



The pore size can be determined by things like reverse size exclusion chromatography that is described by *J.Chromedogr.*, 387(1987) 65, or by a BET (Brunauer-Emmett-Teller) method; however, unless otherwise specifically indicated, the average pore size was determined according to the method as described in *Angw. Chem. Int. Ed. Engl.*, 17. 901-908(1978).

[0045]

First, for determination, the particles to be measured are packed in a column, [this column] is connected to an HPLC apparatus, THF is used as the eluent, and the retention capacity of a plurality of standard polystyrenes and benzenes that cover a wide range of molecular weights are respectively measured. The results are plotted on a graph where the molecular weight  $M$  (easily seen on a logarithmic scale) is graduated on the Y-axis and the retention capacity (mL) is graduated on the X-axis. A curve with the thus obtained respective points smoothly connected is called a calibration curve. The exclusion limit points ( $V_1$ ,  $M_1$ ) are determined by ordinary methods from the calibration curve and the straight line  $X=(V_1+V_2)/2$  is drawn on the graph using the measuring point ( $V_2$ , 78) of benzene with this. The average pore size  $\phi_m[\text{\AA}]$  is calculated by substituting the following Formula (X) in the same way with the empirical formula (11) of the above-mentioned cited reference p. 905 by reading the Y coordinate  $M_m$  of the node (called the average pore point) of the straight line and calibration curve.

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[Equation 2]

$$\phi_m[\text{\AA}] = 0.62 \times (M_m)^{0.59}$$

(X)

[0046]

Further, the "average pore point" is defined by the present inventors. [This] means that the point where the integrated volume from the minimum volume (a size where benzene just fits) becomes 50% when the entire pore volume is 100%. The above equation is used for converting the standard polystyrene equivalent molecular weight of this point to the pore diameter that just fits.

[0047]

### (3) Pellicular Type Ion Exchanger

A pellicular type ion exchanger is a particle that is made by coating a core particle surface with latex with an ion exchange group introduced. The core particle can include [ones like] sulfonated polystyrene.

[0048]

The particle size of an anion exchanger of this invention is desired to be 1-30  $\mu\text{m}$ , more desirably 2-20  $\mu\text{m}$  and, even more desirably, is 2-10  $\mu\text{m}$  for a porous chemical bond type. The particle size of a resin for a pellicular type is ordinarily to an extent of 5-15  $\mu\text{m}$ . The decrease of the theoretical plates of a column is undesirable when the particle size of the anion exchanger exceeds 30  $\mu\text{m}$ , while the increase of column pressure becomes large and packing is extremely difficult when the particle size is less than 1  $\mu\text{m}$ .

The particle size for this invention is a value that is

measured by a Coulter counter (Coulter Counter).

[0049]

(C) Ion Chromatography Use Column

The packing of the anion exchanger of this invention into an ion chromatography-use column is performed according to conventional packing methods like the slurry method. A column pertaining to this invention is used as a high sensitivity suppressor system ion chromatography-use column having alkali-resistant properties.

[0050]

A column that uses an anion exchanger by this invention

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is stable for eluents (ones like a mixed solution of sodium carbonate and sodium hydrogencarbonate, phosphate buffers, aqueous sodium hydroxide solutions and aqueous potassium hydroxide solutions) that are used in suppressor system ion chromatography. In particular, [ones] useful for use by being combined with pH9 or higher, more desirably pH9-13, alkaline eluent, and for use by being combined with a hydroxide type eluent that contains a hydroxide ion as the anion.

[0051]

(D) Anion Measurement Method

An anion measurement method of this invention can be performed according to prior [art] suppressor system ion chromatography.

The total measurement cost can be decreased due to not requiring things like a specific measuring device and concentration

preparations and not requiring the application of high voltage for suppressors due to being under isocratic conditions of a set concentration and being able to utilize a low concentration eluent of 20 mM or less even when using a hydroxide type eluent which previously could not be obtained without using a gradient method or high concentration solutions.

[0052]

In this way, the main anions (phosphate ions, fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, and sulfate ions) can be well separated by the suitable selection of eluent concentration even by using a hydroxide type eluent, not only in the case of carbonic acid type eluent and boric acid type eluent, by utilizing suppressor system ion chromatography-use columns that use an anion exchanger of this invention.

[0053]

Further, an anion measurement method of this invention can simultaneously well separate the main anions (like phosphate ions, fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions and sulfate ions) with halogen oxide ions (like bromate ions, chlorite ions and chlorate ions). When explained in further detail, the separation degree of chlorite ions and bromate ions and the separation degree of chlorite ions and bromide ions can be measured at 1.5 or more even when the above-mentioned ions are simultaneously analyzed. When simultaneously analyzing halogen oxide ions, a suppressor may

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or may not be used.

[0054]

The eluents which can be used for the analysis of halogen oxide ions is not particularly limited in an anion measurement method of this invention and, of course, for a carbonic acid buffer, a hydroxide type eluent like potassium hydroxide or sodium hydroxide can be used; an eluent which is obtained by adjusting the pH of an organic acid like p-hydroxybenzoic acid or phthalic acid from weakly acidic to near neutral can be used in a suppressor system.

[0055]

Thus, [this] is useful for things like trace component analysis in the environment, such as anions in air, water (like river water, tap water, spa water, limnetic water, and drainage), and soil extract solution; analysis of things like food and fertilizer; anion analysis of things like cosmetic raw materials; anion analysis of coating raw materials, coating materials and surface treatment solutions; analysis of ultrapure water, mixed acids, air, lead frames and wafers in the semiconductor field; quality control in the pharmaceutical field; and the analysis of things like circulating water and cooling water at electric power plants. Also, an anion measurement method of this invention is also useful in the analysis of water containing halogen oxide ions as by-products after advanced water treatment purification is done.

[0056]

[Examples]

This invention is explained in further detail by the Examples and Comparative Examples below. However, these are simple representations and this invention is by no means limited to these examples.

[0057]

Example 1:

A poly(vinyl alcohol) type compound that was prepared by the following method was used as the substrate resin with an ion exchanger introduced. A uniformly mixed solution of 100 g of vinyl acetate, 180 g of triallyl isocyanurate, 150 g of butyl acetate and 10 g of 2,2-azobisisobutyronitrile and 1400 mL of water with a small amount of poly(vinyl alcohol) and sodium phosphate dissolved were charged into a 5 L three-necked flask equipped with a reflux condenser and stirred for 10 minutes. Then, a particulate polymer was obtained by performing polymerization for 16 hours at 60°C while stirring under a nitrogen stream. The polymer was filtered, washed and extracted with acetone, then dried.

[0058]

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The obtained polymer and 3 L of aqueous 1 N sodium hydroxide (NaOH) solution were charged into a 5 L three-necked flask equipped with a reflux condenser, a nitrogen inlet tube and a stirrer; saponification of the polymer was performed by stirring for 20 hours at 15°C under a nitrogen stream, then filtered, washed and dried. The density of the hydroxyl group of the poly(vinyl alcohol) polymer that was obtained by saponification was 2.1 meq/g.

An ion exchanger was manufactured by the following procedure with this as a substrate.

[0059]

100 g of the above-mentioned dried polymer, 300 g of 1,4-butanediol diglycidyl ether (referred to as "1,4-BGE" below), 300 mL of dimethylsulfoxide and 65 mL of an aqueous 30 weight% sodium hydroxide solution were charged into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing a glycidyl group containing group to the polymer substrate by stirring for 12 hours at 35°C in a nitrogen stream. After the introduction, the polymer was washed with dimethyl sulfoxide and water, then dried by a vacuum dryer. After drying, the weight of the polymer was 110 g, an increase of 10% more than the original substrate.

[0060]

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 4 g of 1-methylpiperidine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing a tertiary heterocyclic amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and, after being treated for 5 hours at 60°C, was washed and dried. The anion exchanger that was obtained in this way had an average particle size of 5  $\mu$ m and an ion exchange capacity

of 20  $\mu\text{eq/g}$ .

[0061]

An anion exchange column was prepared by packing this anion exchanger into a 4.0 mm internal diameter, 250 mm long polyether ethyl ketone resin (PEEK)-made column. Using a DX-320 [manufactured by Dionex Corporation (*Dionex Corporation*)] equipped with a suppressor as an ion chromatograph, 25  $\mu\text{L}$  of an aqueous solution containing 2 mg/L of  $\text{F}^-$ , 3 mg/L of  $\text{Cl}^-$ , 5 mg/L of  $\text{NO}_2^-$ , 10 mg/L of  $\text{Br}^-$ , 10 mg/L of  $\text{NO}_3^-$ , 15 mg/L of  $\text{SO}_4^{2-}$  and 15 mg/L of  $\text{PO}_4^{3-}$

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was injected in an ion chromatograph as the standard with 15 mM of aqueous sodium hydroxide solution as the eluent flowing at 1.0 mL/min with a column temperature of 35°C. The obtained chromatograph is shown in Figure 2.

[0062]

Example 2:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate resin, which was manufactured in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 1 g of 1-methylpyrrolidine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing a tertiary heterocyclic amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward,



[this] was poured into an aqueous 1 N sodium hydroxide solution and was washed and dried after being treated for 5 hours at 60°C. The anion exchanger which was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same column as in Example 1 and measured in the same manner as in Example 1.

[0063]

Example 3:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate resin, which was prepared in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 10 g of pyridine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing a tertiary heterocyclic amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was poured into an aqueous 1 N sodium hydroxide solution and was washed and dried after being treated for 5 hours at 60°C. The anion exchanger that was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same

column as in Example 1 and measured in the same manner as in Example 1.

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[0064]

Comparative Example 1:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate resin, which was prepared in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was prepared by charging 100 g of glycidyl group containing group introduced polymer, 75 mL of a 1% aqueous trimethylamine solution and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing an aliphatic tertiary amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and was washed and dried after being treated for 5 hours at 60°C. The anion exchanger that was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same column as in Example 1 and measured in the same manner as in Example 1.

[0065]

Comparative Example 2:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate

resin, which was prepared in Example 1 as the substrate, by the same formulation as Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 150 mL of a 1% aqueous triethylamine solution and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer, and introducing an aliphatic tertiary amine by stirring for 1 hour at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was poured into an aqueous 1 N sodium hydroxide solution and was washed and dried after being treated for 5 hours at 60°C. The anion exchanger that was obtained in this way had an average particle size of 5  $\mu\text{m}$  and an ion exchange capacity of approximately 20  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same column as in Example 1 and measured in the same manner as in Example 1.

[0066]

Example 4:

A styrene/divinylbenzene type [resin] manufactured by the following method

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was used as a substrate resin into with an ion exchange group introduced. A uniform mixed solution made from 105 g of 4-acetoxystyrene, 70 g of m-divinylbenzene, 75 g of toluene and 3.5 g of 2,2-azobisisobutyronitrile was suspended in 1250 mL of water

with 10% poly(vinyl alcohol) dissolved and homogenized. Then, [this] was transferred to a 2 L separable flask and a particulate polymer was obtained by performing polymerization for 6 hours at 70°C. The polymer was filtered and washed with water and acetone and 3-6  $\mu\text{m}$  particles were obtained by classification by air separation after air drying.

150 g of the above-mentioned dried polymer was suspended in 1500 mL of methanol and a solution with 150 g of KOH dissolved in 1500 mL of a 50% aqueous methanol solution was added, and [this] was saponified by stirring for 6 hours at 50°C. 135 g of polymer was recovered after washing this with water and acetone, then drying.

[0067]

100 g of the aforementioned dried polymer, 400 g of 1,4-BGE, 300 mL of dimethyl sulfoxide and 65 mL of water were charged into a 2 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and a glycidyl group containing group was introduced to the polymer substrate by stirring for 16 hours at 35°C under a nitrogen stream. After introduction, the polymer was washed with dimethyl sulfoxide and water, then dried with a vacuum dryer. After drying, the mass of the polymer was 105 g and increased 5% more than the original substrate.

[0068]

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 8 g of 1-methylpiperidine and 500 mL of water into a 1 L three-necked flask

equipped with a nitrogen inlet tube and a stirrer, and introducing a tertiary heterocyclic amine by stirring for 4 hours at 40°C. An ion exchanger was obtained by washing according to the same formulation as Example 1.

The anion exchanger obtained above was packed into the same column as in Example 1 and measured in the same manner as in Example 1.

[0069]

Comparative Example 3:

The measurement was performed in the same manner as in Example 1 using a column (pellicular type ion exchanger with a tertiary alkanolamine introduced) that is currently commercially available for hydroxide type eluent use.

[0070]

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Evaluation:

The kind of tertiary amine introduced, the difference in the retention time between the fluoride ion and the water dip, the separation degree of the chloride ion and nitrite ion and the retention time of the phosphate ion are shown in Table 1 for Examples 1-4 and Comparative Examples 1-3. The difference in the retention time between fluoride ion and water dip was determined by using the respective peaks as the retention times. The separation degree R of chloride ion and nitrite ion was determined by the following formula.

[0071]

[Equation 3]

$$R=2X(t_2-t_1)/(w_1+w_2)$$

Here,  $t_1$  and  $t_2$  represent the respective retention times and  $w_1$  and  $w_2$  represent respective peak widths.

[0072]

[Table 1]

	④ 導入した三級アミン	⑤ フッ化物イオンと ウォーターデップの 保持時間差 (分)	⑥ 塩化物イオンと 亜硝酸イオンの 分離度 (R)	⑦ リン酸イオン の 保持時間 (分)
① 実施例 1	1-メチルピペリジン ⑧	1.00	5.2	15.6
① 実施例 2	1-メチルピロリジン ⑨	0.95	5.0	16.2
① 実施例 3	ピリジン ⑩	0.90	5.0	15.8
① 実施例 4	1-メチルピペリジン ⑪	0.85	5.5	19.6
② 比較例 1 (市販品)	アルカノールアミン ⑫	ピークが重なって 測定不能 ⑮	1.8	34.0
③ 比較例 2	トリメチルアミン ⑬	0.79	3.4	16.0
③ 比較例 3	トリエチルアミン ⑭	0.68	3.2	14.1

[Key to Table 1]

- 1 Example 1, 2, etc.
- 2 Comparative Example 1  
(Commercial Product)
- 3 Comparative Example 2, etc.
- 4 Introduced Tertiary Amine

Difference in Retention Time of Fluoride Ion and Water  
Dip (Minutes)

- 6 Separation Degree of Chloride Ion and Nitrite Ion (R)
- 7 Retention Time of Phosphate Ion (Minutes)
- 8 1-methylpiperidine
- 9 1-methylpyrrolidine
- 10 pyridine
- 11 1-methylpiperidine
- 12 alkanolamine
- 13 trimethylamine
- 14 triethylamine
- 15 immeasurable due to overlapping of peaks

[0073]

The retention time of the phosphate ion is extremely long and 30 minutes or more, the fluoride ion is partially overlapped by the water dip, and the separation of the chloride ion and sulfite ion is inadequate by the column, which is currently commercially available, that is shown in Comparative Example 1.

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However, the suppressor system ion chromatograph-use column that uses the anion exchanger which is prepared by introducing a tertiary heterocyclic amine of this invention which is shown in Examples 1, 2 and 3, can adequately separate fluoride ions from the water dip and can also adequately separate chloride ions and nitrite ions even when the retention time of the phosphate ion, which is difficult to elute, is set to 14 to 16 minutes. This shows significant improvement as compared with anion exchangers of

Comparative examples 2 and 3 with acyclic tertiary amine introduced. Further, the substrate resin not being limited to poly(vinyl alcohol) type resins but the introduction of a heterocyclic amine also being effective for other resins is revealed from Example 4.

[0074]

Actual Example 5:

A poly(vinyl alcohol) type polymer that was manufactured by the following method was used as the substrate resin which with an ion exchange group introduced. A uniform mixed solution made from 100 g of vinyl acetate, 180 g of triallyl isocyanurate, 150 g of butyl acetate and 10 g of 2,2-azobisisobutyronitrile and 1400 mL of water with a small amount of poly(vinyl alcohol) and sodium phosphate dissolved were charged into a 5 L three-necked flask equipped with a reflux condenser and stirred for 10 minutes. Then, a particulate polymer was obtained by performing polymerization for 16 hours at 60°C while stirring under a nitrogen stream. The polymer was dried after being filtered, washed and acetone extracted.

[0075]

The obtained polymer and 3 L of an aqueous 1 N sodium hydroxide (NaOH) solution were charged into a 5 L three-necked flask equipped with a reflux condenser, nitrogen inlet tube and stirrer; and, after the polymer was saponified by stirring for 20 hours at 15°C, [it] was filtered, washed and finally dried. The density of the hydroxyl group of the poly(vinyl alcohol) which was



obtained by saponification was 2.1 meq/g. An anion exchanger was made by the following procedure with this as the substrate.

[0076]

100 g of the above-mentioned dried polymer, 300 g of 1,4-BGE, 300 mL of dimethylsulfoxide and 65 mL of an aqueous 30 weight% sodium hydroxide solution were charged into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and introducing a glycidyl group containing group to the polymer substrate by stirring for 12 hours at 35°C under a nitrogen stream. After introduction, the polymer

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was washed with dimethylsulfoxide and water and dried by a vacuum dryer. The mass of the polymer after drying was 110 g and was an increase of 10% more than the original substrate.

[0077]

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 5 g of 1-methylpiperidine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and introducing a tertiary heterocyclic amine by stirring for 2 hours at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution, then washed with water and dried after being treated for 20 hours at 100°C. The anion exchanger that was obtained in this manner had an average particle size of approximately 5  $\mu$ m and an

ion exchange capacity of approximately 30  $\mu\text{eq}$ .

[0078]

An anion exchange column was prepared by packing this anion exchanger into a polyether ether ketone resin (PEEK)-made column of inner diameter 4.0 mm and length 250 mm. An aqueous 3 mM sodium carbonate solution was flowed at 0.7 mL/min as the eluent, at a column temperature of 25°C, using a 761 Compact IC [Metrohm, Ltd (Metrohm Ltd.) product] equipped with a suppressor as an ion chromatograph, and 20  $\mu\text{L}$  of an aqueous solution containing 2 mg/L of  $\text{F}^-$ , 10 mg/L of  $\text{ClO}_2^-$ , 10 mg/L of  $\text{BrO}_3^-$ , 3 mg/L of  $\text{Cl}^-$ , 5 mg/L of  $\text{NO}_2^-$ , 10 mg/L of  $\text{ClO}_3^-$ , 10 mg/L of  $\text{Br}^-$ , 10 mg/L of  $\text{NO}_3^-$ , 15 mg/L of  $\text{SO}_4^{2-}$  and 15 mg/L of  $\text{PO}_4^{3-}$  was injected into the ion chromatograph as a standard. The obtained chromatogram is shown in Figure 3.

[0079]

#### Actual Example 6:

1,4-BGE was introduced into the poly(vinyl alcohol) type substrate resin prepared as a substrate in Example 1 by the same formulation as in Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 1.5 g of 1-methylpyrrolidine and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and introducing a tertiary heterocyclic amine by stirring for 2 hours at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention.

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Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution and washed and dried after being treated for 20 hours at 100°C. The anion exchanger which was obtained in this manner had an average particle size of approximately 5  $\mu\text{m}$  and an ion exchange capacity of approximately 30  $\mu\text{eq/g}$ .

The anion exchanger obtained above was packed into the same column as in Example 5 and measured in the same manner as in Example 1.

[0080]

Comparative Example 4:

1,4-BGE was introduced to a poly(vinyl alcohol) type substrate resin prepared as a substrate in Example 1 by the same formulation as Example 1.

An anion exchanger was manufactured by charging 100 g of glycidyl group containing group introduced polymer, 100 mL of aqueous 1% trimethylamine solution and 500 mL of water into a 1 L three-necked flask equipped with a nitrogen inlet tube and a stirrer and introducing a tertiary heterocyclic amine by stirring for 2 hours at 40°C. This was washed with 1 N hydrochloric acid and an aqueous 1 N sodium hydroxide solution while allowing water intervention. Afterward, [this] was charged into an aqueous 1 N sodium hydroxide solution, then washed with water and dried after being treated for 20 hours at 100°C. The anion exchanger that was obtained in this manner had an average particle size of approximately 5  $\mu\text{m}$  and an ion exchange capacity of approximately 30  $\mu\text{eq}$ .

The anion exchanger obtained above was packed into the same column as in Example 5 and measured in the same manner as in Example 1.

[0081]

Evaluation:

The kind of introduced tertiary amine, the separation degree of chlorite ion and bromate ion, the separation degree of chlorate ions and bromide ion, and the retention time of the sulfate ion are shown in Table 2 for Examples 5 and 6 and Comparative Example 4. The retention time of the sulfate ion is shown in order to show that the 3 various columns can be properly evaluated by agreeing the elution position of the sulfate ion which has the longest retention time. Further, the separation degree R was determined by the following formula.

[0082]

[Equation 4]

$$R=2X(t_2-t_1)/(w_1+w_2)$$

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Here,  $w_1$  and  $w_2$  represent respective peak widths and  $t_1$  and  $t_2$  represent the respective retention times.

The degree of separation R is desired to be 1/5 or more.

[0083]

[Table 2]

		(12)	(13)	(14)	(15)
	導入した三級アミン	亜塩素酸イオンと臭素酸イオンの分離度 (R)	塩素酸イオンと臭化物イオンの分離度 (R)	硫酸イオンの保持時間 (分)	
(9)	実施例 5	1-メチルピペリジン (16)	1. 7 2	2. 1 1	2 5. 2
(10)	実施例 6	1-メチルピロリジン (17)	1. 7 4	1. 5 5	2 5. 5
(11)	比較例 4	トリメチルアミン (18)	1. 5 8	0. 8 0	2 5. 8

[Key to Table 2]

- 9 Example 5
- 10 Example 6
- 11 Comparative Example 4
- 12 Tertiary Amine Introduced
- 13 Separation Degree of Chlorite Ion and Bromate Ion (R)
- 14 Separation Degree of Chlorate Ion and Bromide Ion (R)
- 15 Retention Time of Sulfate Ion (Minutes)
- 16 1-methylpiperidine
- 17 1-methylpyrrolidine
- 18 trimethylamine

[0084]

Adequate separation was understood to be possible at 1.5 or more for both the separation degree of chlorite ions and bromate ions and the separation degree of chlorate ions and bromide ions for a suppressor system ion chromatography-use column which used an anion exchanger that was manufactured by introducing a tertiary heterocyclic amine of this invention that is represented by Examples 5 and 6, compared to the separation degree of chlorate ions and bromide ions being inadequate at less than 1.5 by a prior

[art] suppressor system ion chromatography-use column that used an anion exchanger which was manufactured by a tertiary alkylamine that is represented by Comparative Example 4. This reveals a significant improvement as compared with those with an acyclic tertiary amine introduced which are represented by Comparative Example 4.

[0085]

Further, a chromatogram of an analysis that used a column which was manufactured by Example 5 is shown in Figure 3. It is known that the excellent properties of the porous chemical bond type anion exchanger derived from poly(vinyl alcohol) type substrate can be reflected by the ability to adequately separate fluoride ions and the water dip (a negative peak generated due to water in the sample) and the ability to adequately separate the carbonate dip from other ion peaks.

A carbonic acid buffer is used as the eluent for the examples, but usable eluents for analysis of halogen oxide ions are not limited to this.

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[0086]

[Effects of the Invention]

A suppressor system ion chromatograph use column that is packed with an anion exchanger of this invention reduce the elution time of phosphate ions to 20 minutes or less under an isocratic condition using a low concentration hydroxide type eluent of 20 mM or less, can adequately separate fluoride ions, which are difficult

to retain, from the water dip, and can adequately separate chloride ions and nitrite ions, and can thus shorten the measuring time in analysis that uses the above-mentioned eluent and lengthen the life of the continuous regeneration type ion exchange membrane suppressor.

[0087]

Therefore, this invention is useful in a wide field of things like environment, food, agriculture, cosmetics, coating materials, semiconductor, pharmaceuticals and electric power and is especially useful for the analysis of a number of ppb nitrite ions in the presence of a number of tens of ppm of chloride ions as in tap water analysis and or for the analysis of water that contains halogen oxide ions which is produced as a by-product as in water subjected to advanced water purification.

[0088]

[Simple Explanation of the Figures]

[Figure 1] is a schematic diagram showing a fundamental construction of ion chromatography.

[Figure 2] is a chromatogram that is sampled by injecting a sample aqueous solution that contains seven kinds of standard anions into a separation column prepared by packing an ion exchanger of this invention that is obtained in Example 1.

[Figure 3] is a chromatogram of the simultaneous analysis of halogen oxide ions and the seven kinds of standard anions by a measurement method of this invention that is obtained in Example 5.

[0089]

[Description of Numerical References]

- 1 fluoride ion peak
- 2 chlorite ion peak
- 3 bromide ion peak
- 4 chloride ion peak
- 5 nitrite ion peak
- 6 chloride ion peak
- 7 bromide ion peak
- 8 nitrate ion peak
- 9 phosphate ion peak
- 10 sulfate ion peak

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